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(54) **COMPOSANT DE CATALYSEUR AU PHOSPHINIMINE/
HETEROATOME**
(54) **PHOSPHINIMINE/HETEROATOM CATALYST COMPONENT**

(57) Organometallic complexes having a phosphinimine ligand, a (non-phosphinimine) heteroligand and at least one activatable ligand are catalyst components for olefin polymerization. Preferred polymerization systems are prepared by combining the organometallic complexes with an ionic activator and/or an alumoxane. Preferred catalyst components contain Ti, Zr or Hf and are activated with an ionic activator to provide ethylene polymerization catalysts.

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PHOSPHINIMINE/HETEROATOM CATALYST COMPONENT**ABSTRACT OF THE DISCLOSURE**

30 Organometallic complexes having a phosphinimine ligand, a (non-phosphinimine) heteroligand and at least one activatable ligand are catalyst components for olefin polymerization. Preferred polymerization systems are prepared by combining the organometallic complexes with an ionic activator and/or an alumoxane. Preferred catalyst components contain Ti, Zr or Hf and are activated with an ionic activator to provide ethylene polymerization catalysts.

FIELD OF THE INVENTION

This invention relates to an olefin polymerization catalyst component which is an organometallic complex having a phosphinimine ligand, a heteroatom ligand and at least one activatable ligand. The catalyst component is further characterized by the absence of any cyclopentadienyl ligand.

BACKGROUND OF THE INVENTION

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Certain "metallocenes" (especially bis-cyclopentadienyl complexes of group 4 metals) are highly productive catalysts for olefin polymerization when used in combination with an appropriate activator (see, for example, United States Patent ("USP") 4,542,199 (Sinn *et al*) and USP 5,198,401 (Hlatky and Turner).

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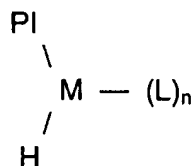
Olefin polymerization catalysts having one cyclopentadienyl ligand and one phosphinimine ligand are disclosed in a commonly assigned patent application (Stephan *et al*).

We have now discovered a family of highly active olefin polymerization catalysts which do not contain a cyclopentadienyl ligand.

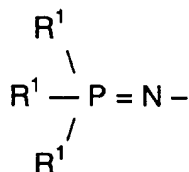
SUMMARY OF THE INVENTION

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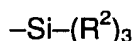
The present invention provides a catalyst component for olefin polymerization which is an unbridged organometallic complex described by the formula:



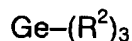
wherein M is a metal selected from group 3-10 metals; PI is a phosphinimine ligand defined by the formula:



wherein each R¹ is independently selected from the group consisting of (a) a hydrogen atom, (b) a halogen atom, (c) C₁₋₂₀ hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, (d) a C₁₋₈ alkoxy radical, (e) a C₆₋₁₀ aryl or aryloxy radical, (f) an amido radical (which may be substituted); (g) a silyl radical of the formula:



wherein each R² is independently selected from the group consisting of hydrogen, a C₁₋₈ alkyl or alkoxy radical, C₆₋₁₀ aryl or aryloxy radicals, and (h) a germanyl radical of the formula:



wherein R² is as defined above; H is a heteroligand characterized by (a) containing a heteroatom selected from N, S, B, O or P, and (b) being bonded to M through a sigma or pi bond with the proviso that H is not a phosphinimine ligand as defined above; L is an activatable ligand; n is 1, 2 or 3 depending upon the valence of M with the proviso that L is not a cyclopentadienyl, indenyl or fluorenyl ligand.

DETAILED DESCRIPTION

1. Description of Catalyst Component

The catalyst component of this invention is unbridged. The term "unbridged" is meant to convey its conventional meaning, namely that

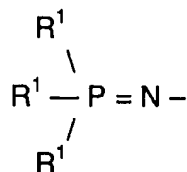
there is not a bridging group which connects the phosphinimine ligand and the heteroatom ligand with formal bonds. (By contrast, many metallocene catalysts having two cyclopentadienyl-type ligands are "bridged" with, for example, a dimethyl silyl "bridge" in which the silicon atom is formally bonded to both of the cyclopentadienyl ligands.) "Unbridged" catalyst components are typically less expensive to synthesize than the corresponding bridged analogues.

1.1 Metals

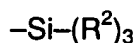
The catalyst component of this invention is an organometallic complex of a group 3, 4, 5, 6, 7, 8, 9 or 10 metal (where the numbers refer to columns in the Periodic Table of the Elements using IUPAC nomenclature). The preferred metals are selected from groups 4 and 5, especially titanium, hafnium, zirconium or vanadium.

1.2 Phosphinimine Ligand

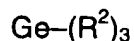
The catalyst component of this invention must contain a phosphinimine ligand which is covalently bonded to the metal. This ligand is defined by the formula:



wherein each R¹ is independently selected from the group consisting of a hydrogen atom, a halogen atom, C₁₋₂₀ hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, a C₁₋₈ alkoxy radical, a C₆₋₁₀ aryl or aryloxy radical, an amido radical, a silyl radical of the formula:



wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and a germanyl radical of the formula:



wherein R^2 is as defined above.

10 The preferred phosphinimines are those in which each R^1 is a hydrocarbyl radical. A particularly preferred phosphinimine is tri-(tertiary butyl) phosphinimine (i.e. where each R^1 is a tertiary butyl group).

1.3 Activatable Ligand

20 The term "activatable ligand" refers to a ligand which may be activated by a cocatalyst (also known as an "activator" to facilitate olefin polymerization. Exemplary activatable ligands are independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-10} hydrocarbyl radical, a C_{1-10} alkoxy radical, a C_{5-10} aryl oxide radical; each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C_{1-8} alkyl radical, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryl oxy radical, an amido radical which is unsubstituted or substituted by up to two C_{1-8} alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to

30 two C_{1-8} alkyl radicals.

The activatable ligands must not be cyclopentadienyl ligands (or related ligands such as indenyl or fluorenyl).

The number of activatable ligands depends upon the valency of the metal and the valency of the activatable ligand. The preferred catalyst

metals are group 4 metals in their highest oxidation state (i.e. 4⁺) and the preferred activatable ligands are monoanionic. Thus, the preferred catalyst components contain a phosphinimine ligand, a heteroatom ligand and two (monoanionic) activatable ligands bonded to the group 4 metal. In some instances, the metal of the catalyst component may not be in the highest oxidation state. For example, a titanium (III) component would contain only one activatable ligand.

1.4 Heteroligand

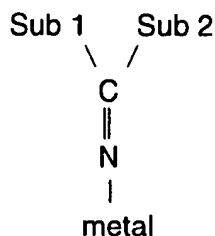
The heteroligand is also essential to this invention. This ligand contains at least one heteroatom selected from the group consisting of boron, nitrogen, oxygen, phosphorus or sulfur. The heteroligand may be sigma or pi-bonded to the metal. Exemplary heteroligands are described in sections 1.4.1 to 1.4.6 below.

1.4.1 Ketimide Ligands

As used herein, the term "ketimide ligand" refers to a ligand which:

- (a) is bonded to the group 4 metal via a metal-nitrogen atom bond;
- (b) has a single substituent on the nitrogen atom, (where this single substituent is a carbon atom which is doubly bonded to the N atom);
and
- (c) has two substituents (Sub 1 and Sub 2, described below) which are bonded to the carbon atom.

Conditions a, b, and c are illustrated below:



The substituents "Sub 1 and Sub 2" may be the same or different. Exemplary substituents include hydrocarbyls having from 1 to 20 carbon atoms; silyl groups, amido groups and phosphido groups. For reasons of cost and convenience it is preferred that these substituents both be hydrocarbyls, especially simple alkyls and most preferably tertiary butyl.

1.4.2 Silicone-Containing Heteroligands

These ligands are defined by the formula:



where the – denotes a bond to the transition metal and μ is sulfur or oxygen.

The substituents on the Si atom, namely R_x , R_y and R_z are required in order to satisfy the bonding orbital of the Si atom. The use of any particular substituent R_x , R_y or R_z is not especially important to the success of this invention. It is preferred that each of R_x , R_y and R_z is a C_{1-4} hydrocarbyl group such as methyl, ethyl, isopropyl or tertiary butyl (simply because such materials are readily synthesized from commercially available materials).

1.4.3 Amido Ligands

The term "amido" is meant to convey its broad, conventional meaning. Thus, these ligands are characterized by (a) a metal-nitrogen

bond, and (b) the presence of two substituents (which are typically simple alkyl or silyl groups) on the nitrogen atom.

1.4.4 Alkoxy Ligands

The term "alkoxy" is also intended to convey its conventional meaning. Thus these ligands are characterized by (a) a metal oxygen bond, and (b) the presence of a hydrocarbyl group bonded to the oxygen atom. The hydrocarbyl group may be a ring structure and/or substituted (e.g. 2, 6 di-tertiary butyl phenoxy).

1.4.5 Boron Heterocyclic Ligands

These ligands are characterized by the presence of a boron atom in a closed ring ligand. This definition includes heterocyclic ligands which also contain a nitrogen atom in the ring. These ligands are well known to those skilled in the art of olefin polymerization and are fully described in the literature (see, for example, USPs 5,637,659; 5,554,775 and the references cited therein).

1.4.6 Phosphole Ligands

The term "phosphole" is also meant to convey its conventional meaning. "Phosphole" is also meant to convey its conventional meaning. "Phospholes" are cyclic dienyl structures having four carbon atoms and one phosphorus atom in the closed ring. The simplest phosphole is C_4PH_4 (which is analogous to cyclopentadiene with one carbon in the ring being replaced by phosphorus). The phosphole ligands may be substituted with, for example, C_{1-20} hydrocarbyl radicals (which may, optionally, contain halogen substituents); phosphido radicals; amido radicals; silyl or alkoxy radicals.

Phosphole ligands are also well known to those skilled in the art of olefin polymerization and are described as such in USP 5,434,116 (Sone, to Tosoh).

2. Description of Activators (or "Cocatalysts")

The catalyst components described in part 1 above are used in combination with an "activator" (which may also be referred to by a person skilled in the art as a "cocatalyst") to form an active catalyst system for olefin polymerization. Simple aluminum alkyls and alkoxides may provide comparatively weak cocatalytic activity under certain mild polymerization conditions. However, the preferred activators are alumoxanes and so-called ionic activators, as described below.

2.1 Alumoxanes

The alumoxane activator may be of the formula:



wherein each R^4 is independently selected from the group consisting of C_{1-20} hydrocarbyl radicals and m is from 0 to 50, preferably R^4 is a C_{1-4} alkyl radical and m is from 5 to 30. Methylalumoxane (or "MAO") is the preferred alumoxane.

Alumoxanes are well known as activators for metallocene-type catalysts.

Activation with alumoxane generally requires a molar ratio of aluminum in the activator to (group 4) metal in the catalyst from 20:1 to 1000:1. Preferred ratios are from 50:1 to 250:1.

2.2 Ionic Activators

Ionic activators are also well known for metallocene catalysts. See, for example, USP 5,198,401 (Hlatky and Turner). These compounds may be selected from the group consisting of:

- (i) compounds of the formula $[R^5]^+ [B(R^7)_4]^-$ wherein B is a boron atom, R^5 is a cyclic C_{5-7} aromatic cation or a triphenyl methyl cation and each R^7 is independently selected from the group consisting of phenyl radicals which are unsubstituted or substituted with from 3 to 5 substituents selected from the group consisting of a fluorine atom, a C_{1-4} alkyl or alkoxy radical which is unsubstituted or substituted by a fluorine atom; and a silyl radical of the formula $-Si-(R^9)_3$; wherein each R^9 is independently selected from the group consisting of a hydrogen atom and a C_{1-4} alkyl radical; and
- (ii) compounds of the formula $[(R^8)_t ZH]^+ [B(R^7)_4]^-$ wherein B is a boron atom, H is a hydrogen atom, Z is a nitrogen atom or phosphorus atom, t is 2 or 3 and R^8 is selected from the group consisting of C_{1-8} alkyl radicals, a phenyl radical which is unsubstituted or substituted by up to three C_{1-4} alkyl radicals, or one R^8 taken together with the nitrogen atom may form an anilinium radical and R^7 is as defined above; and
- (iii) compounds of the formula $B(R^7)_3$ wherein R^7 is as defined above.

In the above compounds preferably R^7 is a pentafluorophenyl radical, and R^5 is a triphenylmethyl cation, Z is a nitrogen atom and R^8 is a C_{1-4} alkyl radical or R^8 taken together with the nitrogen atom forms an anilium radical which is substituted by two C_{1-4} alkyl radicals.

The "ionic activator" may abstract one or more activatable ligands so as to ionize the catalyst center into a cation but not to covalently bond with the catalyst and to provide sufficient distance between the catalyst and the ionizing activator to permit a polymerizable olefin to enter the resulting active site.

Examples of ionic activators include:

- 10 triethylammonium tetra(phenyl)boron,
- tripropylammonium tetra(phenyl)boron,
- tri(n-butyl)ammonium tetra(phenyl)boron,
- trimethylammonium tetra(p-tolyl)boron,
- trimethylammonium tetra(o-tolyl)boron,
- tributylammonium tetra(pentafluorophenyl)boron,
- tripropylammonium tetra (o,p-dimethylphenyl)boron,
- 20 tributylammonium tetra(m,m-dimethylphenyl)boron,
- tributylammonium tetra(p-trifluoromethylphenyl)boron,
- tributylammonium tetra(pentafluorophenyl)boron,
- tri(n-butyl)ammonium tetra (o-tolyl)boron
- N,N-dimethylanilinium tetra(phenyl)boron,
- N,N-diethylanilinium tetra(phenyl)boron,
- 30 N,N-diethylanilinium tetra(phenyl)n-butylboron,
- N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron
- di-(isopropyl)ammonium tetra(pentafluorophenyl)boron,
- dicyclohexylammonium tetra (phenyl)boron
- triphenylphosphonium tetra(phenyl)boron,
- tri(methylphenyl)phosphonium tetra(phenyl)boron,

tri(dimethylphenyl)phosphonium tetra(phenyl)boron,
 tropillium tetrakis(pentafluorophenyl) borate,
 triphenylmethylium tetrakis(pentafluorophenyl) borate,
 benzene (diazonium) tetrakis(pentafluorophenyl) borate,
 tropillium phenyltris-pentafluorophenyl borate,
 triphenylmethylium phenyl-trispentafluorophenyl borate,
 10 benzene (diazonium) phenyltrispentafluorophenyl borate,
 tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
 triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
 tropillium tetrakis (3,4,5-trifluorophenyl) borate,
 benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
 20 tropillium tetrakis (1,2,2-trifluoroethenyl) borate,
 triphenylmethylium tetrakis (1,2,2-trifluoroethenyl) borate,
 benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl) borate,
 tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate,
 triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate, and
 benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate.

Readily commercially available ionic activators include:

30 N,N- dimethylaniliumtetrakis(pentafluorophenyl) borate;
 triphenylmethylium tetrakis(pentafluorophenyl) borate; and
 trispentafluorophenyl borane.

3. Homogeneous or Heterogeneous Catalyst

The catalyst system of this invention may be used in a
 homogeneous form in solution polymerization (where the term

"homogeneous" means that the catalyst and cocatalyst/activator are soluble in, or miscible with, the polymerization solvent). However, when the catalyst is employed in a slurry or gas phase polymerization, it is highly preferred to use the catalyst in a heterogeneous or "supported form". It is also highly preferred that the catalyst does not cause reactor fouling. The art of preparing heterogeneous catalysts which do not lead to reactor fouling is not adequately understood, though it is generally accepted that the catalytic material should be very well anchored to the support so as to reduce the incidence of fouling resulting from the deposition of catalyst or cocatalyst which has dissociated from the support.

In general, heterogeneous catalysts may be grouped into three main categories:

3.1. Unsupported Alumoxane/Catalyst Mixtures

These catalysts may be easily prepared by evaporating the solvent or diluent from a liquid mixture of an alumoxane and the catalyst component. The resulting product is a solid at room temperature due to the comparatively high molecular weight of the alumoxane. There are two disadvantages to this approach, namely cost (i.e. alumoxanes are comparatively expensive – and the alumoxane is used as an expensive "support" material) and "reaction continuity/fouling" (i.e. the alumoxane may partially melt under polymerization conditions, leading to reactor instability/fouling). United States Patent (USP) 4,752,597 (Turner, to Exxon) illustrates this approach for the preparation of a heterogeneous catalyst.

3.2. Metal Oxide Supported Catalysts

These catalysts are prepared by depositing the catalyst component and a cocatalyst on a very porous metal oxide support. The catalyst and cocatalyst are substantially contained within the pore structure of the metal oxide particle. This means that a comparatively large metal oxide particle is used (typically particle size of from 40 to 80 microns). The preparation of this type of supported catalyst is described in USP 4,808,561 (Welborn, to Exxon).

3.3. Filled/Spray Dried Catalysts

This method of catalyst preparation is also well known. For example, USPs 5,648,310; 5,674,795 and 5,672,669 (all to Union Carbide) teach the preparation of a heterogeneous catalyst by spray drying a mixture which contains a metallocene catalyst, an alumoxane cocatalyst and a "filler" which is characterized by having a very small particle size (less than one micron) and by being unreactive with the catalyst and cocatalyst. The examples illustrate the use of very fine particle size "fumed" silica which has been treated to reduce the concentration of surface hydroxyls. The resulting catalysts exhibit good productivity. Moreover, they offer the potential to provide a catalyst which is not prone to "hot spots" (as the catalyst may be evenly distributed, at low concentration, throughout the heterogeneous matrix). However, these catalysts suffer from the potential disadvantage of being very friable because they are prepared with a fine, "inert" filler material which does not react with / anchor to the catalyst or cocatalyst.

Friable catalyst particles lead to the formation of "fines" in the polyethylene product, and may also aggravate reactor fouling problems.

An alternative approach is the preparation of spray dried catalysts using a hydrotalcite as a "reactive" filler (as opposed to the unreactive filler described in the above-mentioned USP to Union Carbide). This method of catalyst preparation is described in more detail in a commonly assigned patent application. Either approach is suitable for use with the catalysts of this invention.

4. Polymerization Processes

The catalysts of this invention are suitable for use in any conventional olefin polymerization process, such as the so-called "gas phase", slurry", "high pressure" or "solution" polymerization processes.

The use of a heterogenous catalyst is preferred for gas phase and slurry processes whereas a homogeneous catalyst is preferred for the solution process.

The polymerization process according to this invention uses ethylene and may include other monomers which are copolymerizable therewith such as other alpha olefins (having from three to ten carbon atoms, preferably butene, hexene or octene) and, under certain conditions, dienes such as hexadiene isomers, vinyl aromatic monomers such as styrene or cyclic olefin monomers such as norbornene.

The present invention may also be used to prepare elastomeric co- and terpolymers of ethylene, propylene and optionally one or more diene monomers. Generally, such elastomeric polymers will contain about 50 to about 75 weight % ethylene, preferably about 50 to 60 weight % ethylene

and correspondingly from 50 to 25 % of propylene. A portion of the monomers, typically the propylene monomer, may be replaced by a conjugated diolefin. The diolefin may be present in amounts up to 10 weight % of the polymer although typically is present in amounts from about 3 to 5 weight %. The resulting polymer may have a composition comprising from 40 to 75 weight % of ethylene, from 50 to 15 weight % of propylene and up to 10 weight % of a diene monomer to provide 100 weight % of the polymer. Preferred but not limiting examples of the dienes are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene. Particularly preferred dienes are 5-ethylidene-2-norbornene and 1,4-hexadiene.

The polyethylene polymers which may be prepared in accordance with the present invention typically comprise not less than 60, preferably not less than 70 weight % of ethylene and the balance one or more C₄₋₁₀ alpha olefins, preferably selected from the group consisting of 1-butene, 1-hexene and 1-octene. The polyethylene prepared in accordance with the present invention may be linear low density polyethylene having density from about 0.910 to 0.935 g/cc. The present invention might also be useful to prepare polyethylene having a density below 0.910 g/cc - the so-called very low and ultra low density polyethylenes.

The most preferred polymerization process of this invention encompasses the use of the novel catalysts (together with a cocatalyst) in a medium pressure solution process. As used herein, the term "medium pressure solution process" refers to a polymerization carried out in a solvent for the polymer at an operating temperature from 100 to 320°C

(especially from 120 to 220°C) and a total pressure of from 3 to 35 mega Pascals. Hydrogen may be used in this process to control (reduce) molecular weight. Optimal catalyst and cocatalyst concentrations are affected by such variables as temperature and monomer concentration but may be quickly optimized by non-inventive tests.

Further details concerning the medium pressure polymerization process are well known to those skilled in the art and widely described in the open and patent literature.

The catalyst of this invention may also be used in a slurry polymerization process or a gas phase polymerization process.

The typical slurry polymerization process uses total reactor pressures of up to about 50 bars and reactor temperature of up to about 200°C. The process employs a liquid medium (e.g. an aromatic such as toluene or an alkane such as hexane, propane or isobutane) in which the polymerization takes place. This results in a suspension of solid polymer particles in the medium. Loop reactors are widely used in slurry processes. Detailed descriptions of slurry polymerization processes are widely reported in the open and patent literature.

In general, a fluidized bed gas phase polymerization reactor employs a "bed" of polymer and catalyst which is fluidized by a flow of monomer which is at least partially gaseous. Heat is generated by the enthalpy of polymerization of the monomer flowing through the bed. Unreacted monomer exits the fluidized bed and is contacted with a cooling system to remove this heat. The cooled monomer is then re-circulated through the polymerization zone together with "make-up" monomer to

replace that which was polymerized on the previous pass. As will be appreciated by those skilled in the art, the "fluidized" nature of the polymerization bed helps to evenly distribute/mix the heat of reaction and thereby minimize the formation of localized temperature gradients (or "hot spots"). Nonetheless, it is essential that the heat of reaction be properly removed so as to avoid softening or melting of the polymer (and the resultant-and highly undesirable - "reactor chunks"). The obvious way to maintain good mixing and cooling is to have a very high monomer flow through the bed. However, extremely high monomer flow causes undesirable polymer entrainment.

An alternative (and preferable) approach to high monomer flow is the use of an inert condensable fluid which will boil in the fluidized bed (when exposed to the enthalpy of polymerization), then exit the fluidized bed as a gas, then come into contact with a cooling element which condenses the inert fluid. The condensed, cooled fluid is then returned to the polymerization zone and the boiling/condensing cycle is repeated.

The above-described use of a condensable fluid additive in a gas phase polymerization is often referred to by those skilled in the art as "condensed mode operation" and is described in additional detail in USP 4,543,399 and USP 5,352,749. As noted in the '399 reference, it is permissible to use alkanes such as butane, pentanes or hexanes as the condensable fluid and the amount of such condensed fluid preferably does not exceed about 20 weight per cent of the gas phase.

Other reaction conditions for the polymerization of ethylene which are reported in the '399 reference are:

Preferred Polymerization Temperatures: about 75°C to about 115°C (with the lower temperatures being preferred for lower melting copolymers - especially those having densities of less than 0.915 g/cc - and the higher temperatures being preferred for higher density copolymers and homopolymers); and

Pressure: up to about 1000 psi (with a preferred range of from about 100 to 350 psi for olefin polymerization).

The '399 reference teaches that the fluidized bed process is well adapted for the preparation of polyethylene but further notes that other monomers may be employed – as is the case in the process of this invention.

EXAMPLES

The invention will now be illustrated in further detail by way of the following non-limiting examples. For clarity, the Examples have been divided into three parts, namely Part A (Catalyst Component Synthesis), Part B (Solution Polymerization) and Part C (Gas Phase Polymerization).

Polymer Analysis

Gel permeation chromatography ("GPC") analysis was carried out using a commercially available chromatograph (sold under the name Waters 150 GPC) using 1,2,4-trichlorobenzene as the mobile phase at 140°C. The samples were prepared by dissolving the polymer in the mobile phase solvent in an external oven at 0.1% (weight/volume) and were run without filtration. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% and 5.0% for the number average molecular weight (Mn) and weight average

molecular weight (Mw), respectively. Melt index (MI) measurements were conducted according to ASTM method D-1238-82.

Polymer densities were measured using pressed plaques (ASTM method D-1928-90), with a densitometer.

The following abbreviations are used in the Examples:

^tBu = tertiary butyl (e.g. ^tBu₃ = tri-tertiary butyl)

Me = methyl

Et = ethyl

¹H NMR = proton nuclear magnetic resonance

ⁱPr = isopropyl

Ph = phenyl

Mw = weight average molecular weight

Mn = number average molecular weight

PD = polydispersity (or Mw/Mn)

PE = polyethylene

Cat = catalyst

Hr = hour

M = molar

PART A Catalyst Component Synthesis

A.1 Synthesis of (^tBu₃PN)TiCl₃

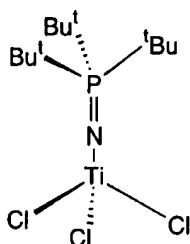
Method 1:

(^tBu₃PN)₂TiCl₂ (0.22 g, 0.3992 mmol, prepared by refluxing a mixture of 2 moles ^tBu₃P=NSiMe₃ + 1 mole TiCl₄ in toluene) and TiCl₄ (75 mg, 0.3992 mmol) was refluxed in toluene (10 mL) for about 3 hours. An almost colorless solution formed, which was pumped to dryness to give

the product in quantitative yield. ^1H NMR (toluene- d_8 , δ): 1.088 (d, $^3J_{\text{P-H}} = 14$ Hz).

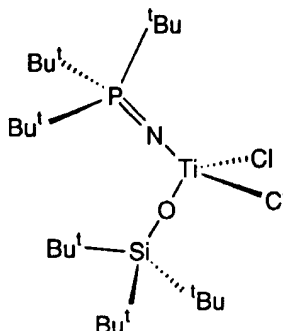
Method 2:

To a toluene (25 mL) solution of TiCl_4 (0.19g, 1mmol) at -78°C was added slowly a mixture of $^t\text{Bu}_3\text{P}=\text{NH}$ (0.22 g, 1 mmol) and Et_3N (0.1 g, 1 mmol) in toluene (25 mL). The orange color of the solution faded immediately. The solution was slowly warmed to room temperature, stirred for a couple of hours and was filtered at 60°C to remove the white precipitate (Et_3NHCl). The filtrate was evaporated under vacuum to dryness to give the product as white crystalline solid. Yield: 95%. The same NMR data as above.



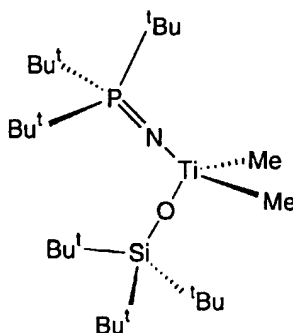
A.2 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{SiO})\text{TiCl}_2$

$\text{NaOSi}^t\text{Bu}_3$ (387 mg, 1.626 mmol) in toluene (20 mL) was added to a cold (-78°C) toluene solution (20mL) of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (603 mg, 1.626 mmol). The solution was warmed to room temperature, stirred for 2 hours and was pumped to dryness. The solid was redissolved in hexane and the hexane solution was filtered. The filtrate was slowly pumped to dryness to give shiny colorless crystals of the product (895 mg, 100% yield). ^1H NMR (toluene- d_8 , δ): 1.345(s, 27H), 1.17(d, 13.6 Hz, 27H).



A.3 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{SiO})\text{TiMe}_2$

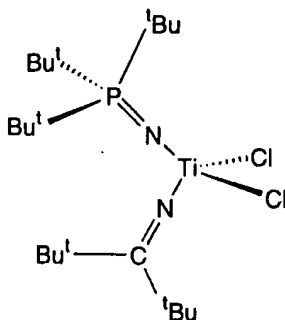
To a toluene solution (~20mL) of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{SiO})\text{TiCl}_2$ (0.641 g, 1.164 mmol) at -78°C was added a 3M diethyl ether solution of MeMgBr (1 mL, 3mmol). The reaction mixture was warmed to room temperature, stirred for 2 hours and pumped to dryness. The solid was extracted with hexane (3x15 mL) and the hexane extract was slowly evaporated to dryness. Colorless crystals of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{SiO})\text{TiMe}_2$ were obtained (0.592 mg, ~100% yield). ^1H NMR (toluene- d_8 , δ): 1.363(s, 27H), 1.251(d, $J = 13.2\text{Hz}$, 27H), 0.936(s, 6H).



A.4 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_2\text{CN})\text{TiCl}_2$

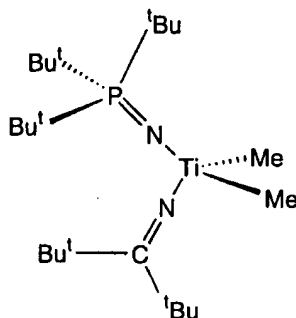
$^t\text{Bu}_2\text{CNLi}$ (0.168 g, 1.141 mmol) in toluene (20 mL) was added to a toluene solution (20 mL) of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ at -78°C . The solution was warmed to room temperature and was stirred for 1 hour. An orange solution formed, which was pumped to dryness and was redissolved in

hexane (20 mL). The hexane solution was filtered and the filtrate was slowly evaporated to dryness. Orange crystals of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_2\text{CN})\text{TiCl}_2$ (0.542 g, 100% yield) was obtained. ^1H NMR (toluene- d_8 , δ): 1.283(s, 18H), 1.204(d, $J = 13.8\text{Hz}$, 27H).



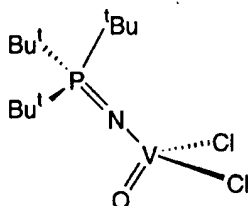
A.5 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_2\text{CN})\text{TiMe}_2$

To a solution of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_2\text{CN})\text{TiCl}_2$ (0.350 g, 0.736 mmol) in toluene at -78°C was added a diethyl ether solution (3M) of MeMgBr (0.8 mL, 2.4 mmol). The orange color of the solution faded to light orange immediately. The solution was warmed to room temperature, stirred for 1 hour and pumped to dryness. The solid was extracted with hexane (3 x 15 mL) and the hexane extract was slowly evaporated under vacuum to dryness. The product was obtained as light orange crystals (0.317g, 99% yield). ^1H NMR (toluene- d_8 , δ): 1.353(s, 18H), 1.263(d, $J = 12.8\text{Hz}$, 27H), 0.828(s, 6H).



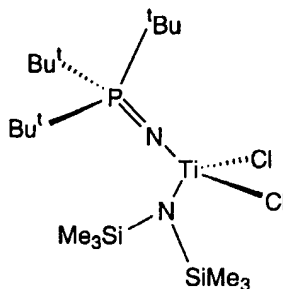
A.6 Synthesis of $(^t\text{Bu}_3\text{PN})\text{VOCl}_2$

$^t\text{Bu}_3\text{PNSiMe}_3$ (1.02 g, 3.52 mmol) in toluene (10 mL) was added to a toluene solution (50 mL) of VOCl_3 (0.610 g, 3.52 mmol) at -78°C . The red color of the solution did not fade until it was heated to 100°C for 1 hour. An orange solution formed with a tiny amount of green tar on the wall of the flask. After 2 hours at 100°C , the light orange solution was transferred into another flask to separate from the green tar and was pumped slowly to dryness. Orange crystalline material (1.1g, 88% yield) was obtained. ^1H NMR (toluene- d_8 , δ): 1.16 (d, $J = 14$ Hz).



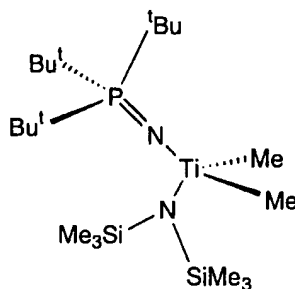
A.7 Synthesis of $(^t\text{Bu}_3\text{PN})[\text{N}(\text{SiMe}_3)_2]\text{TiCl}_2$

A hexane solution (10 mL) of $\text{LiN}(\text{SiMe}_3)_2$ (0.167g, 1 mmol) was slowly added to a suspension of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (0.37g, 1 mmol) in hexane (50mL) at -78°C . The mixture was then warmed to room temperature. After stirring for 12 hours, all volatiles were removed under vacuum. The residue was dissolved in hexane and LiCl was removed by filtration. The product crystallized as yellow crystals from a concentrated hexane solution at -35°C . Yield: 85%. ^1H NMR in (toluene- d_8 , δ): 1.23 (d, $^3J_{\text{P-H}} = 13.7$ Hz, 27H, Bu^t); 0.57 (s, 18H, SiCH_3).



A.8 Synthesis of (^tBu₃PN) [N(SiMe₃)₂]TiMe₂

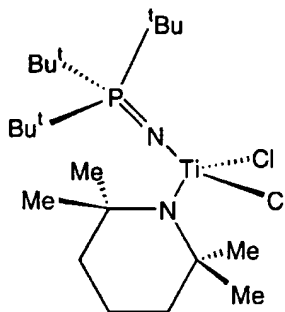
To a toluene (50 mL) solution of (^tBu₃PN)[N(SiMe₃)₂]TiCl₂ (0.1 g, 0.2 mmol) at -78°C was added slowly a diethyl ether solution of MeMgBr (3M, 0.15mL, 0.45 mmol). The system was then warmed to room temperature and a slurry formed. After 2 hours at room temperature with stirring, all volatiles were removed under vacuum and the residue was extracted with hexane. The product crystallized as yellowish crystals from hexane at -35°C. Yield: 75%. ¹H NMR in (toluene-d₈, δ): 1.27 (d, ³J_{P-H}=12.4 Hz, 27H, Bu^t); 1.16 (s, 6H, TiCH₃); 0.57 (s, 18H, SiCH₃).



A.9 Synthesis of (^tBu₃PN)(2,2,6,6-tetramethylpiperidinyl)TiCl₂

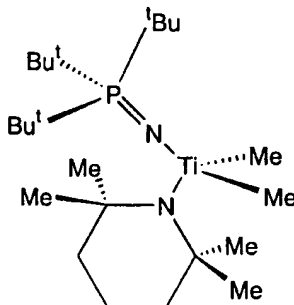
To a hexane (50 mL) suspension of (^tBu₃PN)TiCl₃ (0.74 g, 2 mmol) at -78°C was added slowly a hexane (20 mL) solution of 2,2,6,6-tetramethylpiperidinyl-lithium (0.294g, 2 mmol). The system was then warmed to room temperature. A yellow solution formed. After 12 hours at room temperature with stirring, all volatiles were removed under vacuum. The residue was dissolved in hexane and the solution was filtered to

remove LiCl. The yellow crystalline product was obtained by crystallization at -35°C in hexane. Yield: 78%. ^1H NMR in (toluene- d_8 , δ): 1.31 (d, $^3J_{\text{P-H}}=13.9$ Hz, 27H, Bu^t); 1.94 (s, 12H, NCCH_3); 1.36 (s, br, 6H, CH_2).



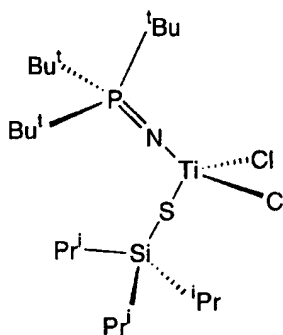
A.10 Synthesis of $(^t\text{Bu}_3\text{PN})(2,2,6,6\text{-tetramethylpiperidinyl})\text{TiMe}_2$

A diethyl ethyl solution of MeMgBr (3M, 1 mL, 3 mmol) was added to a toluene (50 mL) solution of $(^t\text{Bu}_3\text{PN})(2,2,6,6\text{-tetramethylpiperidinyl})\text{TiCl}_2$ (0.3 g, 0.63 mmol) at -78°C . The solution was warmed to room temperature and was stirred for 2 hours. A light yellow slurry formed, which was pumped to dryness and the residue was extracted with hexane. The hexane extract was concentrated and the product crystallized at -35°C . Yield: 85%. ^1H NMR in (toluene- d_8 , δ): 1.33 (d, $^3J_{\text{P-H}}=12.8$ Hz, 27H, Bu^t); 1.81 (s, 12H, NCCH_3); 1.25 (s, br, 6H, CH_2); 0.92 (s, 6H, TiMe).

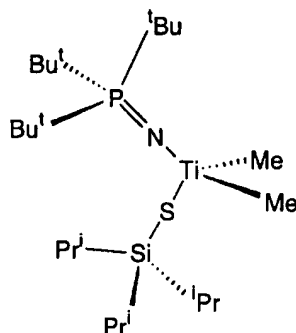


A.11 Synthesis of $(^t\text{Bu}_3\text{PN})(^i\text{Pr}_3\text{SiS})\text{TiCl}_2$

To a hexane (50 mL) suspension of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (0.37 g, 1 mmol) was added slowly a hexane (20 mL) solution of $^i\text{Pr}_3\text{SiSLi}$ (0.195g, 1 mmol) at -78°C . The solution was warmed to room temperature, stirred for 12 hours and was filtered. Yellow crystals were obtained from a concentrated hexane solution at -35°C . Yield: 90%. ^1H NMR in (toluene- d_8 , δ): 1.19 (d, $^3J_{\text{P-H}}=13.9$ Hz, 27H, Bu^t); 1.32 (d, $^3J_{\text{C-H}}=6.9$ Hz, 18H, $i\text{-Pr}$); 1.32 (m, 3H, $i\text{-Pr}$).

**A.12 Synthesis of $(^t\text{Bu}_3\text{PN})(^i\text{Pr}_3\text{SiS})\text{TiMe}_2$**

A diethyl ether solution of MeMgBr (3M, 0.47 mL, 1.4 mmol) was added to a toluene (50 mL) solution of $(^t\text{Bu}_3\text{PN})(^i\text{Pr}_3\text{SiS})\text{TiCl}_2$ (0.4 g, 0.7 mmol) at -78°C . The solution was warmed to room temperature and was stirred for 2 hours. The yellow solution became an almost colorless slurry, which was then pumped to dryness. The residue was dissolved in hexane and the solution was filtered. The product was obtained by crystallization at -35°C from hexane. Yield: 76%. ^1H NMR in (toluene- d_8 , δ): 1.23 (d, $^3J_{\text{P-H}}=13.0$ Hz, 27H, Bu^t); 1.14 (d, $^3J_{\text{C-H}}=5.1$ Hz, 18H, $i\text{-Pr}$); 1.05 (br, 3H, $i\text{-Pr}$). 1.08 (s, 6H, TiMe).



A.13 Synthesis of $\text{LiOC}(\text{}^t\text{Bu}_2)(\text{CH}_2\text{PPh}_2)$

10 To a hexane solution (40 milliliters (mL)) of $\text{}^t\text{Bu}_2\text{CO}$ (0.867 grams (g), 6.1 millimoles (mmol)) was slowly added $\text{Ph}_2\text{PCH}_2\text{Li}(\text{tmeda})$ (1.97 g, 6.1 mmol) (tmeda = tetramethylethylenediamine) in 20 mL of hexane (*J. Chem. Soc., Chem. Commun*, 220, 1984). The pale yellow solution was then stirred for 16 hours. The solution was then cooled and concentrated (~10 mL) under reduced pressure and placed in a freezer to

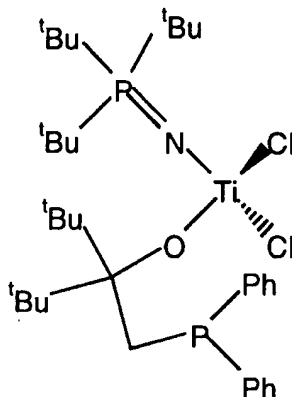
20 crystallize the product. Isolated yield of the off-white solid was 1.5 g (71%). Proton nuclear magnetic resonance spectrum (^1H NMR) in deuterated toluene (C_7D_8): 7.6-7.06 (peak area = 10 protons) (m, 10H), 2.88 (d, $J = 8.4$ Hz, 2H) and 1.17 (s, 18H).

A.14 Synthesis of $(\text{}^t\text{Bu}_3\text{PN})[(\text{Ph}_2\text{PCH}_2)(\text{}^t\text{Bu}_2)\text{CO}]\text{TiCl}_2$

To a solution of $(\text{}^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (0.729 g, 1.97 mmol) in 40 mL of toluene at -78°C was added dropwise $\text{LiOC}(\text{}^t\text{Bu}_2)(\text{CH}_2\text{PPh}_2)$ (0.686 g, 1.97 mmol) in 20 mL of toluene. The solution was then allowed to reach

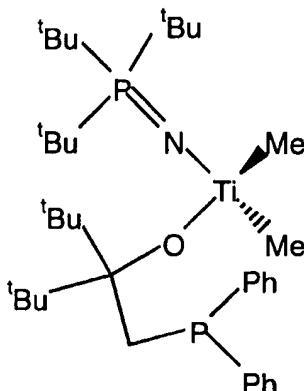
30 room temperature while stirring for 16 hours. The pale yellow solution was then filtered and the solvent was removed under reduced pressure. The yellow solid was then re-crystallized from toluene/hexane to give an off-white solid. Isolated yield was 1.2g (90%). ^1H NMR (toluene- d_8 , δ): 7.80

(m, 5H), 7.10 (m, 5H), 3.02 (d, $J = 7.2$ Hz, 2H), 1.31 (s, 18H) and 1.26 (d, $J = 13.4$ Hz, 27H).



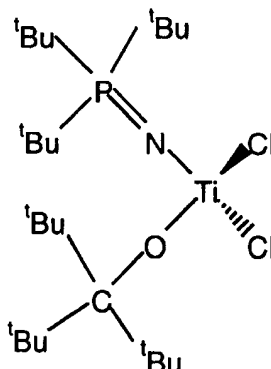
A.15 Synthesis of $(^t\text{Bu}_3\text{PN})[(\text{Ph}_2\text{PCH}_2)(^t\text{Bu}_2\text{CO})\text{TiMe}_2]$

To a solution of $(^t\text{Bu}_3\text{PN})[(\text{Ph}_2\text{PCH}_2)(^t\text{Bu}_2\text{CO})\text{TiCl}_2]$ (0.315 g, 0.466 mmol) in 20 mL of toluene at -78°C was added using a syringe MeMgBr (3M in diethyl ether) (0.4 mL, 1.2 mmol). The solution was then allowed to reach room temperature while stirring for 1 hour. All toluene was then removed under reduced pressure. The white solid was slurried in fresh toluene (2 x 15 mL) and filtered to give a clear-colorless solution. Toluene was removed under reduced pressure leaving an off-white crystalline solid. Isolated yield was 0.25 g (93%). ^1H NMR (toluene- d_8 , δ): 7.67 (m, 5H), 7.10 (m, 5H), 2.99 (d, $J = 6$ Hz, 2H), 1.35 (s, 18H), 1.31 (d, $J = 13.3$ Hz, 27H), and 0.95 (s, 6H).

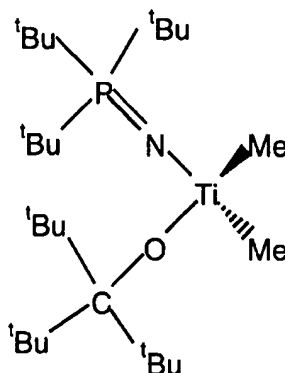


A.16 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{CO})\text{TiCl}_2$

To a solution of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (0.301 g, 0.813 mmol) in 40 mL of toluene at -78°C was added dropwise $^t\text{Bu}_3\text{COLi}$ (0.168 g, 0.813 mmol) (*Polyhedron*, 14(22), 3335-3362, 1995) in 20 mL of toluene. The solution was then allowed to reach room temperature while stirring for 16 hours. The colorless solution was then filtered and the filtrate was evaporated to dryness under reduced pressure leaving a white crystalline solid. Isolated yield was 0.378 g (87%). ^1H NMR (toluene- d_8 , δ): 1.53 (s, 27H) and 1.22 (d, $J = 13.6$ Hz, 27H).

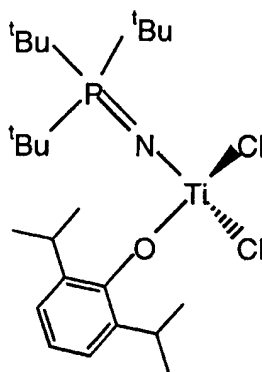
**A.17 Synthesis of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{CO})\text{TiMe}_2$**

To a solution of $(^t\text{Bu}_3\text{PN})(^t\text{Bu}_3\text{CO})\text{TiCl}_2$ (0.195 g, 0.365 mmol) in 15 mL of toluene at -78°C was added using a syringe 3M MeMgBr in diethyl ether (0.32 mL, 0.96 mmol). The solution was then allowed to reach room temperature while stirring for 16 hours. All toluene was then removed under reduced pressure. The white solid was slurried in hexane (2 x 15 mL) and filtered to give a clear-colorless solution. Hexane was removed under reduced pressure leaving a white crystalline solid. Yield was quantitative. ^1H NMR (toluene- d_8 , δ): 1.53 (s, 27H), 1.29 (d, $J = 12.9$ Hz, 27H) and 0.93 (s, 6H).



A.18 Synthesis of $(^t\text{Bu}_3\text{PN})(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{O})\text{TiCl}_2$

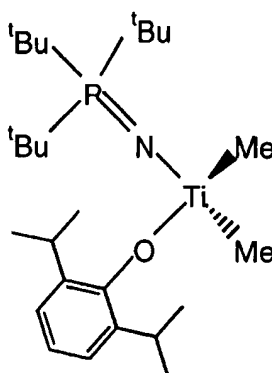
To a solution of $(^t\text{Bu}_3\text{PN})\text{TiCl}_3$ (0.368 g, 0.994 mmol) in 40 mL of toluene at -78°C was added dropwise 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{OLi}$ (0.183 g, 0.994 mmol) in 20 mL of toluene. The solution was then allowed to reach room temperature while stirring for 16 hours. The yellow-orange solution was then filtered and the filtrate was evaporated to dryness under reduced pressure leaving an orange crystalline solid. Isolated yield was 0.465 g (91%). ^1H NMR (toluene- d_6 , δ): 7.1 (d, 2H), 6.98 (t, 1H), 3.87 (sept., 2H), 1.36 (d, $J = 6.9$ Hz, 12H) and 1.04 (d, $J = 13.9$ Hz, 27H).



A.19 Synthesis of $(^t\text{Bu}_3\text{PN})(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{O})\text{TiMe}_2$

To a solution of $(^t\text{Bu}_3\text{PN})(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{O})\text{TiCl}_2$ (0.149 g, 0.291 mmol) in 15 mL of toluene at -78°C was added using a syringe 3M MeMgBr in diethyl ether (0.194 mL, 0.582 mmol). The solution was then allowed to

reach room temperature while stirring for 1 hour. After the solution was pumped to dryness, the white solid was slurried in hexane (2 x 15 mL) and filtered to give a clear colorless solution. Hexane was removed under reduced pressure leaving a pale yellow oil which crystallized upon standing. Yield was quantitative. ^1H NMR (toluene- d_8 , δ): 7.1 (d, 2H), 6.98 (t, 1H), 3.77 (sept., 2H), 1.36 (d, $J = 6.8$ Hz, 12H), 1.14 (d, $J =$
 10 13.1 Hz, 27H) and 1.08 (s, 6H).



20 **A.20 Synthesis of (tri-t-butylphosphinimine)(tetramethylphospholyl)titanium dichloride**

(Tetramethylphospholyl)titanium trichloride (1g, 3.4 mmol) and tri-t-butylphosphinimine-N-trimethylsilyl (985 mg, 3.5 mmol) were combined as solids and toluene (20 mL) was then added. The reaction was heated to 90°C for 4 hours and then the toluene was removed in vacuo. The
 30 resulting orange solid was washed hexane (10 mL) and pumped dry under vacuum. Yield 1.31g. ^1H (C_7D_8): 2.27 (d, $J_{\text{P-H}} = 9.9$ Hz), 2.18 (s), 1.26 (d, $J_{\text{P-H}} = 13.6$ Hz).

A.21 Synthesis of (tri-t-butylphosphinimine)(tetramethylphospholyl)titanium dimethyl

(tri-t-butylphosphinimine)(tetramethylphospholyl)titanium dichloride (355 mg, 0.75 mmol) was slurried in ether (30mL) at 10°C and MeMgBr

(1.5 ml of a 3M solution in ether) was added dropwise. The reaction was warmed to room temperature, stirred for 5 minutes and then the solvent was removed in vacuo. The product was extracted with hexane, the reaction filtered and the hexane removed in vacuo to leave the product as a pale yellow solid. Isolated Yield, 220 mg. ^1H (C_7D_8): 2.16 (s), 2.05 (d, $J_{\text{P-H}} = 9.9$ Hz), 1.33 (d, $J_{\text{P-H}} = 12.9$ Hz), 0.29 (s).

10 **PART B Solution Polymerization**

Solution polymerizations were completed either in a Solution Batch Reactor ("SBR") or in a continuous reaction. The "SBR" experiments are described in Part B.1 and the continuous experiments in Part B.2.

B.1 SBR Experimental Conditions

20 The SBR uses a programmable logical control (PLC) system with Wonderware 5.1 software for process control. Ethylene polymerizations were performed in a 500 mL Autoclave Engineers Zipperclave reactor equipped with an air driven stirrer and an automatic temperature control system. All the chemicals were fed into the reactor batchwise except ethylene which was fed on demand.

Typical experimental conditions for screening experiments are tabulated below.

30

Cyclohexane	216 mL
Catalyst Concentration	200 $\mu\text{mol/L}$
Activator	210 $\mu\text{mol/L}$
Scavenger	<ul style="list-style-type: none"> • PMAO-IP 1 mmol/L put into the reactor with 216 mL reaction solvent. • PMAO-IP 1 mmol/L dissolved in 250 mL of cyclohexane as the scavenger, the solution was stirred for 10 minutes at room temperature, then withdrawn with a canula before the reaction solvent was loaded in
Reaction Temperature	160°C
Reactor Pressure	140 psig total
Stirring Speed	2000 rpm
Comonomer	10 or 20 mL of octene

10

Notes:

1. Table B.1 identifies the borane or borate activator used in each experiment.
2. "PMAO-IP" is a commercially available methylalumoxane.

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TABLE B.1

Run #	Catalyst	Activator	Activity (g PE/ mmol {cat} Hr)	Mw (*10 ⁻³) and PD
10396	^t Bu ₃ PN(^t Bu ₃ SiO)TiMe ₂ (1)	[CPh ₃][B(C ₆ F ₅) ₄]	957.8	67.6 (3.9)
10418	^t Bu ₃ PNTiN(SiMe ₃) ₂ Me ₂ (2)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	1847.6	183.9(3.4)
10421	^t Bu ₃ PNTiMe ₂ NC ^t Bu ₂ (3)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	2030.9	162.7(3.0)
10425	^t Bu ₃ PNTiMe ₂ (O-C ^t Bu ₂ CH ₂ PPH ₂) (4)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	85.2	
10426	^t Bu ₃ PN(tetramethylpiperidinyl)TiMe ₂ (5)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	2178.5	136.2 (2.4)

Run #	1-octene (mL)	Catalyst	Activator	Activity (g PE/ mmol {cat} Hr)	Mw (*10 ⁻³) and PD
10422	20	^t Bu ₃ PNTiMe ₂ NC ^t Bu ₂ (3)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	503.8	27.4 (1.9)
10427	20	^t Bu ₃ PN(tetramethylpiperidinyl) TiMe ₂ (5)	[NHMe ₂ Ph][B(C ₆ F ₅) ₄]	1913.5	18.5 (2.3)

Notes:

- (1) Catalyst from Part A, Section A.3
- (2) Catalyst from Part A, Section A.8
- (3) Catalyst from Part A, Section A.5
- (4) Catalyst from Part A, Section A.15
- (5) Catalyst from Part A, Section A.10

B.2 Continuous Solution Polymerization

All the polymerization experiments described below were conducted on a continuous solution polymerization reactor. The process is continuous in all feed streams (solvent, monomers and catalyst) and in the removal of product. All feed streams were purified prior to the reactor by contact with various absorption media to remove catalyst killing impurities such as water, oxygen and polar materials as is known to those skilled in the art. All components were stored and manipulated under an atmosphere of purified nitrogen.

All the examples below were conducted in a reactor of 71.5 cc internal volume. In each experiment the volumetric feed to the reactor was kept constant and as a consequence so was the reactor residence time.

The catalyst solutions were pumped to the reactor independently and there was no pre-contact between the activator and the catalyst. Because of the low solubility of the catalysts, activators and MAO in cyclohexane, solutions were prepared in purified xylene. The catalyst was activated *in situ* (in the polymerization reactor) at the reaction temperature in the presence of the monomers. The polymerizations were carried out in cyclohexane at a pressure of 1500 psi. Ethylene was supplied to the reactor by a calibrated thermal mass flow meter and was dissolved in the reaction solvent prior to the polymerization reactor. If comonomer (for example 1-octene) was used it was also premixed with the ethylene before entering the polymerization reactor. Under these conditions the ethylene

conversion is a dependent variable controlled by the catalyst concentration, reaction temperature and catalyst activity etc.

The internal reactor temperature is monitored by a thermocouple in the polymerization medium and can be controlled at the required set point to +/- 0.5 C. Downstream of the reactor the pressure was reduced from the reaction pressure (1500 psi) to atmospheric. The solid polymer was then recovered as a slurry in the condensed solvent and was dried by evaporation before analysis.

The ethylene conversion was determined by a dedicated on-line gas chromatograph by reference to propane which was used as an internal standard. The average polymerization rate constant was calculated based on the reactor hold-up time, the catalyst concentration in the reactor and the ethylene conversion and is expressed in l/(mmol*min). Average polymerization rate (k_p) = $(Q/(100-Q)) \times (1/[TM]) \times (1/HUT)$, where:

Q is the percent ethylene conversion;

[TM] is the catalyst concentration in the reactor expressed in mM;

and

HUT is the reactor hold-up time in minutes.

Polymer Analysis

Melt index (MI) measurements were conducted according to ASTM method D-1238-82.

Polymer densities were measured on pressed plaques (ASTM D-1928-90) with a densitometer.

Example 1

(C₄Me₄P)TiNP(^tBu)₃Me₂ (from Part A, section A.22) was added to the reactor at 37.0×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.00 (mol/mol). The reaction temperature was 160°C and 1.0 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 91.1% was observed (see table B.2).

10 **Example 2**

(C₄Me₄P)TiNP(^tBu)₃Me₂ (from Part A, section A.22) was added to the reactor at 27.8×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.00 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. In addition 5.0 ml/min of 1-octene was also added to the reactor. An ethylene conversion of 89.6% was observed (see table B.2).

20 **Example 3**

(^tBu)₃PNTiOSi(^tBu)₃Me₂ (from Part A, section A.3) was added to the reactor at 2.3×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.00 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 98.9% was observed (see table B.2).

30 **Example 4**

(^tBu)₃PNTiOSi(^tBu)₃Me₂ (from Part A, section A.3) was added to the reactor at 2.3×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.00 (mol/mol). The reaction temperature was 180°C and 3.3 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 94.3% was observed (see table B.2).

Example 5

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 3.0×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 0.77 (mol/mol). The reaction temperature was 200°C and 3.8 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 90.9% was observed (see table B.2).

10 **Example 6**

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 4.9×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 0.5 (mol/mol). The reaction temperature was 200°C and 3.8 gram/min of ethylene was continuously added to the reactor. In addition 3.0 ml/min of 1-octene was also fed to the reactor. An ethylene conversion of 88.4% was observed (see table B.2).

20 **Example 7**

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 2.3×10^{-6} mol/l along with MAO (MMAO-7 Akzo-Nobel) at Al/Ti = 200 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of approximately 13% was observed (see table B.2).

30 **Example 8**

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 2.3×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 1.00 (mol/mol) and MAO (MMAO-7 Akzo Nobel) Al/Ti = 7.5 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was

continuously added to the reactor. An ethylene conversion of 90.1% was observed (see table B.2).

Example 9

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 2.8×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 1.00$ (mol/mol) and MAO (MMAO-7 Akzo Nobel) $\text{Al/Ti} = 7.5$ (mol/mol).

10 The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. In addition 1.0 ml/min of 1-octene was also added to the reactor. An ethylene conversion of 90.7% was observed (see table B.2).

Example 10

$(^t\text{Bu})_3\text{PNTiOSi}(^t\text{Bu})_3\text{Me}_2$ (from Part A, section A.3) was added to the reactor at 3.4×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 0.8$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 88.2% was observed (see table B.2).

Example 16

$(^t\text{Bu})_3\text{PNTiNC}(^t\text{Bu})_2\text{Me}_2$ (from Part A, section A.5) was added to the reactor at 11.6×10^{-6} mol/l along with $\text{HNMe}_2\text{Ph B}(\text{C}_6\text{F}_5)_4$ (Akzo Nobel) at $\text{B/Ti} = 1.0$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 90.3% was observed (see table B.2).

Example 17

$(^t\text{Bu})_3\text{PNTiNC}(^t\text{Bu})_2\text{Me}_2$ (from Part A, section A.5) was added to the reactor at 11.6×10^{-6} mol/l along with $\text{HNMe}_2\text{Ph B}(\text{C}_6\text{F}_5)_4$ (Akzo Nobel) at

B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. In addition 3.0 ml/min of 1-octene was added. An ethylene conversion of 89.4% was observed (see table B.2).

Example 18

(^tBu)₃PNTiNC(^tBu)₂Me₂ (from Part A, section A.5) was added to the reactor at 11.6×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 89.0% was observed (see table B.2).

Example 19

(^tBu)₃PNTiNC(^tBu)₂Me₂ (from Part A, section A.5) was added to the reactor at 13.9×10^{-6} mol/l along with Ph₃C B(C₆F₅)₄ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. In addition 3.0 ml/min of 1-octene was added. An ethylene conversion of 88.3% was observed (see table B.2).

Comparative Example 20

(C₅Me₅)₂ZrCl₂ (purchased from Strem) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 140°C and 1.0 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 55.5% was observed (see table B.3).

Comparative Example 21

(C₅Me₅)₂ZrCl₂ (Strem) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 160°C and 1.0 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 35.6% was observed (see table B.3).

10 **Comparative Example 22**

(C₅Me₅)₂ZrCl₂ (Strem) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 37.4% was observed (see table B.3).

20 **Comparative Example 23**

rac-Et(ind)₂ZrCl₂ (purchased from Witco) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene was continuously added to the reactor. An ethylene conversion of 94.6 % was observed (see table B.3).

Comparative Example 24

30 rac-Et(ind)₂ZrCl₂ (Witco) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 160°C and 2.1 gram/min of ethylene and 3.25 ml/min of 1-octene was continuously added to the reactor. An ethylene conversion of 94.8% was observed (see table B.3).

TABLE B.2

Example	Total flow to reactor (ml/min)	Catalyst concentration (mol/l x 10 ⁶)	Ethylene conversion (%)	Calculated polymerization rate (kp) (l/mmol X min)	Polymer density (g/cc)	Polymer melt index	Mn x 10 ⁻³	Mw x 10 ⁻³
1	27.0	37.0	91.1	105	0.956	0.80	-	-
2	27.0	27.8	89.6	117	-	27.0	-	-
3	27.0	2.3	98.9	14533	-	-	44.3	169.1
4	27.0	2.3	94.3	2679	0.942	0.05	20.2	95.3
5	27.0	3.0	90.9	1247	0.947	1.26	18.9	57.3
6	27.0	4.9	88.4	594	0.887	2900	-	-
7	27.0	2.3	13	24	-	-	-	-
8	27.0	2.3	90.1	1476	0.942	0.004	38.5	116.4
9	27.0	2.8	90.7	1324	0.905	83.3	12.9	33.4
10	27.0	3.4	88.6	870	0.942	0.006	31.0	79.7
16	27.0	11.6	90.3	303	-	-	-	-
17	27.0	11.6	89.4	276	-	-	-	-
18	27.0	11.6	89.0	263	-	-	-	-
19	27.0	13.9	88.3	205	-	-	-	-

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TABLE B.3

Example	Total flow to reactor (ml/min)	Catalyst concentration (mol/l x 10 ⁵)	Ethylene conversion (%)	Calculated polymerization rate (kp) (l/mmol X min)	Polymer density (g/cc)	Polymer melt index	Mn x 10 ⁻³	Mw x 10 ⁻³
20	27.0	37.0	55.5	13	-	880	2.7	10.0
21	27.0	37.0	35.6	6	-	-	1.8	7.5
22	27.0	37.0	37.4	6	-	620	3.3	12.0
23	27.0	37.0	94.6	179	-	1300	3.9	14.0
24	27.0	37.0	94.8	186	0.925	very high	2.6	10.0

PART C: Gas Phase Polymerization**Catalyst Preparation and Polymerization Testing Using a Semi-Batch, Gas Phase Reactor**

The catalyst preparation methods described below employ typical techniques for the syntheses and handling of air-sensitive materials. Standard Schlenk and drybox techniques were used in the preparation of the supported catalysts. Solvents were purchased as anhydrous materials and further treated to remove oxygen and polar impurities by contact with a combination of activated alumina, molecular sieves and copper oxide on silica/alumina. Where appropriate, elemental compositions of the supported catalysts were measured by Neutron Activation analysis and a reported accuracy of $\pm 1\%$ (weight basis).

The supported catalysts were prepared by initially supporting MAO on a silica support, followed by deposition of the catalyst component.

All the polymerization experiments described below were conducted using a semi-batch, gas phase polymerization reactor of total internal volume of 2.2 L. Reaction gas mixtures, including separately ethylene or ethylene/butene mixtures, were measured in the reactor on a continuous basis using a calibrated thermal mass flow meter, following passage through purification media as described above. A pre-determined mass of the catalyst sample was added to the reactor under the flow of the inlet gas with no pre-contact of the catalyst with any reagent, such as a catalyst activator. The catalyst was activated *in situ* (in the polymerization reactor) at the reaction temperature in the presence of the monomers, using a metal alkyl complex which has been previously

added to the reactor to remove adventitious impurities. Purified and rigorously anhydrous sodium chloride was used as a catalyst dispersing agent.

The internal reactor temperature was monitored by a thermocouple in the polymerization medium and can be controlled at the required set point to $\pm 1.0^{\circ}\text{C}$. The duration of the polymerization experiment was one hour. Following the completion of the polymerization experiment, the polymer was separated from the sodium chloride and the yield determined.

Table C illustrates data concerning the Al/transition metal ratios of the supported catalyst; polymer yield and polymer properties.

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TABLE C

Complex	mmol complex	Support [*]	mg of catalyst	Yield g	gPe/g metal	gPe/g catalyst	Al/M ratio
$[N=P(Bu)_3]Ti(Me_2)(Bu_3SiO)$ (A)	51 mg (0.1004 mmol)	1.001	38	2.2	12091	57.9	92.38
$[N=P(Bu)_3]Ti(Cl_2)[N=C(Bu_2)]$ (B)	24 mg (0.0505 mmol)	0.499	38	1.4	7695	36.8	91.56
$[N=P(Bu)_3]Ti(Cl_2)[N(SiMe_3)]$ (C)	25 mg (0.0504 mmol)	0.501	38	0.2	1099	5.3	92.11

¹ Support is silica treated with MAO (purchased from Witco)² Ethylene-Butene copolymerization (Co) 4 mol. % 1-Butene³ Pe = Polyethylene

Notes:

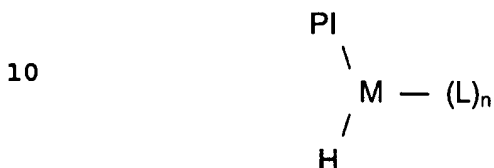
(A) Catalyst from Part A, Section A.3

(B) Catalyst from Part A, Section A.4

(C) Catalyst from Part A, Section A.7

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A catalyst component for olefin polymerization which is an unbridged organometallic complex described by the formula:



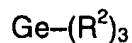
wherein M is a metal selected from group 3-10 metals; PI is a phosphinimine ligand defined by the formula:



wherein each R¹ is independently selected from the group consisting of (a) a hydrogen atom, (b) a halogen atom, (c) C₁₋₂₀ hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, (d) a C₁₋₈ alkoxy radical, (e) a C₆₋₁₀ aryl or aryloxy radical, (f) an amido radical; (g) a silyl radical of the formula:



wherein each R² is independently selected from the group consisting of hydrogen, a C₁₋₈ alkyl or alkoxy radical, C₆₋₁₀ aryl or aryloxy radicals, and (h) a germanyl radical of the formula:



wherein R² is as defined above; H is a heteroligand characterized by (a) containing a heteroatom selected from N, S, B, O or P, and (b) being

bonded to M through a sigma or pi bond with the proviso that H is not a phosphinimine ligand as defined above; L is an activatable ligand; n is 1, 2 or 3 depending upon the valence of M with the proviso that L is not a cyclopentadienyl, indenyl or fluorenyl ligand.

10 2. The catalyst component according to claim 1 wherein said M is selected from group 4 and group 5 metals.

20 3. The catalyst component according to claim 2 wherein each L is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C₁₋₁₀ hydrocarbyl radical, a C₁₋₁₀ alkoxy radical, a C₅₋₁₀ aryl oxide radical; each of which said hydrocarbyl, alkoxy, and aryl oxide radicals may be unsubstituted by or further substituted by a halogen atom, a C₁₋₈ alkyl radical, a C₁₋₈ alkoxy radical, a C₆₋₁₀ aryl or aryl oxy radical, an amido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals; a phosphido radical which is unsubstituted or substituted by up to two C₁₋₈ alkyl radicals.

30 4. The catalyst component according to claim 3 wherein M is titanium (III) and L is 1.

5. The catalyst component according to claim 1 wherein each R¹ is independently a hydrocarbyl group containing from one to twenty carbon atoms.

6. The catalyst component according to claim 1 wherein each R₁ is tertiary-butyl.

7. The catalyst component according to claim 1 wherein said heteroligand is defined by the formula:



wherein R₇, R₈ and R₉ are each independently a C_{1 to 4} hydrocarbyl.

8. An olefin polymerization catalyst system comprising a catalyst component according to claim 1 and an activator.

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9. The catalyst system according to claim 8 wherein said activator is an alumoxane.

10. The catalyst system according to claim 9 wherein said R¹ is tertiary butyl, said M is titanium, n is 2 and each L is a halide.

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11. The catalyst system according to claim 8 wherein said activator is an ionic activator.

12. The catalyst system according to claim 11 wherein each of said R¹ is tertiary butyl, said M is titanium, said heteroligand is an amido or

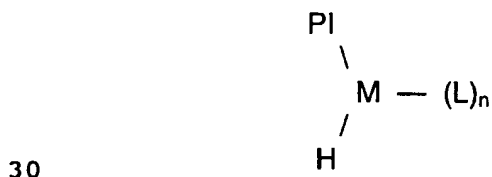
substituted amido, n is 2 and each of said L is a hydrocarbyl group having from one to twenty carbon atoms.

10 13. The catalyst system according to claim 11 wherein said ionic activator comprises an organometallic boron complex containing one boron atom and at least three perfluorinated phenyl ligands bonded to said boron atom.

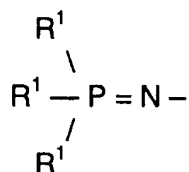
14. The catalyst system according to claim 12 wherein each of said L is methyl.

20 15. A process for the polymerization of ethylene and optionally, a minor amount of at least one additional alpha olefin having from three to ten carbon atoms, characterized in that said process is conducted in the presence of:

(a) a catalyst component for olefin polymerization which is an unbridged organometallic complex described by the formula:



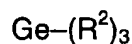
wherein M is a metal selected from group 3-10 metals; PI is a phosphinimine ligand defined by the formula:



wherein each R^1 is independently selected from the group consisting of (a) a hydrogen atom, (b) a halogen atom, (c) C_{1-20} hydrocarbyl radicals which are unsubstituted by or further substituted by a halogen atom, (d) a C_{1-8} alkoxy radical, (e) a C_{6-10} aryl or aryloxy radical, (f) an amido radical, (g) a silyl radical of the formula:



wherein each R^2 is independently selected from the group consisting of hydrogen, a C_{1-8} alkyl or alkoxy radical, C_{6-10} aryl or aryloxy radicals, and (h) a germanyl radical of the formula:



20 wherein R^2 is as defined above; H is a heteroligand characterized by (a) containing a heteroatom selected from N, S, B O or P, and (b) being bonded to M through a sigma or pi bond with the proviso that H is not a phosphinimine ligand as defined above; L is an activatable ligand; n is 1, 2 or 3 depending upon the valence of M with the proviso that L is not a cyclopentadienyl, indenyl or fluorenyl ligand; and

(b) an activator.

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16. The process according to claim 15 wherein said activator is an ionic activator.

17. The process according to claim 16 where said ionic activator comprises an organometallic boron complex containing one boron atom

and at least three perfluorinated phenyl ligands bonded to said boron atom.

18. The process according to claim 15 when undertaken under medium pressure solution polymerization conditions at a temperature of from 100 to 320°C and a pressure of from 3 to 35 mega Pascals.

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19. The process according to claim 18 wherein said metal is titanium (IV), said phosphinimine ligand is tri(tertiary-butyl) phosphinimine and said activator is an ionic activator comprising an organometallic boron complex containing one boron atom and at least three perfluorinated phenyl ligands bonded to said boron atom.

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